Appendices Content

Table

Figures

Appendix A Method for Converting TOC by Combustion to TOC by Oxidation

Background

California Department of Water Resources' Bryte Chemical Laboratory analyzed all Municipal Water Quality Investigations (MWQI) Program samples for organic carbon during the 3-year reporting period. For the past 15 years, both total and dissolved organic carbon (TOC and DOC) in water samples have been determined by a wet oxidation method (oxidation) (Agee 2000 pers comm). Beginning November 2000 Bryte changed its TOC method from wet oxidation to a combustion method. The method change was prompted by the concern of some Bryte laboratory customers that the oxidation method may under-report TOC during peak TOC events (that is, during storm runoff events). During the reporting period, TOC for MWQI samples was determined by the oxidation method from August 1998 through October 2000 and by the combustion method from November 2000 through September 2001. DOC was determined by the oxidation method during the entire 3-year reporting period.

The combustion method generally measures a greater portion of the TOC in a sample than does the oxidation method. Combustion converts most combustible organic carbon to gaseous carbon dioxide; TOC concentrations are derived from the amount of carbon dioxide produced during combustion. In contrast, the oxidation method, which uses chemical oxidation, is generally less powerful than the combustion method especially for samples with elevated particulate organic carbon. Initial exploratory studies suggest that TOC values by combustion were generally 10% to 15% higher than TOC values by oxidation (Agee 2000 pers comm). Greater differences were found in more recent MWQI TOC analyses. Although the combustion method generally measures more TOC than does the oxidation method, both methods measure only a fraction of the organic carbon. The relative advantage of one method over the other is under debate. Because statistical analysis could not be made with TOC data from 2 different methods, TOC values by combustion were transformed to their approximate TOC values by oxidation through a conversion process outlined below. The data used for this analysis are available online or on a CD-ROM (see Appendix B).

Appendix B Report and Data in Electronic Format

Approach

Bryte analyzed a small number of water samples collected from 11 MWQI stations by both oxidation and combustion methods prior to fully implementing the combustion method in November 2001. This small data set alone was insufficient for deriving a reliable statistical relationship because most data were collected from September to October of 2000, which were dry months. The data set was not representative of data for the entire 3-year period. A reliable predictive relationship requires a larger data set with samples collected during both dry and wet months. Therefore, a total of 281 MWQI samples analyzed for TOC by both oxidation and combustion methods from September 2000 through August 2002 were retrieved for this analysis, in addition to the smaller data set collected September to October of 2000. Of the 281 samples, a total of 21 samples were excluded from this analysis. Seventeen of the 21 samples were excluded because of possible erroneous data for TOC combustion. These samples generally contained low DOC. TOC by oxidation was slightly higher than DOC, but TOC by combustion was 3 to 6 times higher than DOC with a median of 6.6 mg/L. The other 4 samples were eliminated because TOC values by oxidation were lower than DOC.

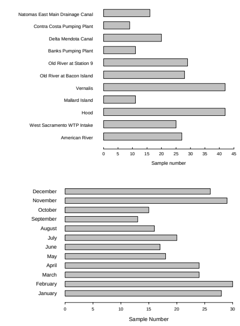


Figure A-1 Sample distribution by station and by month

The 260 samples included in this analysis represent 11 MWQI stations (Figure A-1). No sample was analyzed for TOC using both TOC methods for the 2 MWQI agricultural drainage stations. This didn't affect the analysis because no TOC combustion data from these 2 sites needed conversion. Samples were collected weekly at both San Joaquin River near Vernalis and Sacramento River at Hood. Thus, proportionately more data came from these 2 sites (Figure A-1). Of the 260 samples included in this analysis, 99 samples (38%) were collected during the dry months (May to October), and 161 were collected during the wet months (Figure A-1).

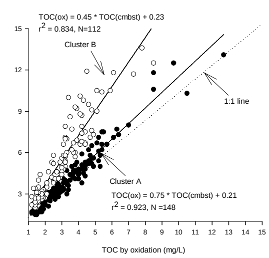


Figure A-2 TOC (combustion) vs. TOC (oxidation): Data clusters and regression equations for conversion

The relationship between TOC by oxidation and by combustion appears to have been linear (Figure A-2); however, the data split into 2 distinct clusters, suggesting that a single regression equation was inadequate to describe the relationship for all the data. The cluster with relatively less scattering and running slightly above and roughly parallel to the 1:1 line (Cluster A) represented samples having TOC by combustion just slightly higher than TOC by oxidation. The other cluster with much greater data dispersion (Cluster B) represented samples with TOC by combustion much higher than TOC by oxidation. A considerable portion of the samples in Cluster A was collected during the dry months, but the majority of samples in Cluster B was taken during the wet months. As mentioned in Chapter 4, organic carbon levels could fall back to baseline levels between rain events during the wet months. Thus, sample collection time alone cannot cleanly separate the 2 clusters.

Further examination of the 2 clusters suggests that the ratio between TOC by combustion and DOC (TOC(cmbst)/DOC) was characteristic of each data cluster. By roughly separating the 2 clusters through visual examination, TOC(cmbst)/DOC ratio in Cluster A ranged from 0.93 to 1.53 with only 4 samples outside this range; TOC(cmbst)/DOC ratio in Cluster B varied between 1.52 and 2.98. Based on these observations, a TOC(cmbst)/DOC ratio of 1.5 was arbitrarily chosen to separate the 2 clusters for regression analysis. Although it was an arbitrary choice, this ratio was an adequate one. For samples with TOC(cmbst)/DOC ratios of 1.5 or less, TOC by combustions is at most 50% higher than DOC. Since TOC by oxidation is generally higher than DOC but lower than TOC by combustion, the ratio of TOC by oxidation over DOC will be less than 1.5. These samples were generally samples with little or no particulate organic carbon (POC). The differences between TOC by combustion and TOC by oxidation were generally small. However, samples with a TOC(cmbst)/DOC ratio of 1.5 or more were generally samples containing high POC. For these samples, TOC by combustion was invariably much higher than TOC by oxidation. For example, the TOC by combustion values for Cluster B samples could be from 1.5 to nearly 3 times as high as TOC by oxidation.

When the 260 data values were separated by a TOC(cmbst)/DOC ratio of 1.5, Cluster A contained 148 samples; and Cluster B, 112 samples. Of all the samples in Cluster A, 10 samples had a TOC(cmbst)/DOC of 1.0 or less suggesting that TOC by combustion is either the same or less than DOC. TOC by combustion was occasionally less than DOC due to normal analytical error. These data are valid because they are within the acceptable error range as specified in the *Quality Assurance Manual* (Fong 2002).

The relationship between TOC by combustion and TOC by oxidation were both linear and statistically significant (Figure A-2). For samples in Cluster A, the linear relationship can be described by the following equation:

$$TOC(ox) = 0.75 * TOC(cmbst) + 0.21 \ (r^2 = 0.923)$$

The regression for samples in Cluster B is

$$TOC(ox) = 0.45 * TOC(cmbst) + 0.23 \ (r^2 = 0.834).$$

Data Conversion

The conversion followed a 2-step process. First, the TOC(cmbst)/DOC ratio of all samples that needed to be converted was computed. Extremely high or low values due to laboratory error were excluded. Then an adequate equation was applied to each sample. For samples having TOC(cmbst)/DOC ratios of 1.5 or less, the equation derived from Cluster A

$$TOC(ox) = 0.75 * TOC(cmbst) + 0.21$$

was used to convert TOC by combustion into TOC by oxidation. Some TOC by combustion data within the group was taken as TOC by oxidation without conversion. These samples typically had a TOC(cmbst)/DOC of less than 1.15 and low TOC values. Conversion may result in the TOC being lower than the DOC. For samples having TOC(cmbst)/DOC ratios of 1.5 or more (up to about 3), the equation developed from Cluster B

$$TOC(ox) = 0.45 * TOC(cmbst) + 0.23$$

was applied. However, for samples with TOC combustion values of less than 2.5, conversion with this equation may result in TOC being lower than DOC. When this occurred, the other equation was applied despite the TOC(cmbst)/DOC indicating otherwise. This is appropriate because considerable data overlap occurred when TOC was lower than about 2 mg/L (Figure A-2).

Of the 725 TOC by oxidation analyses included in this report, 132 or 18% were estimated from TOC by combustion. The distribution of estimated TOC are summarized in Table A-1. The data sets are available online or on a CD-ROM (see Appendix B).

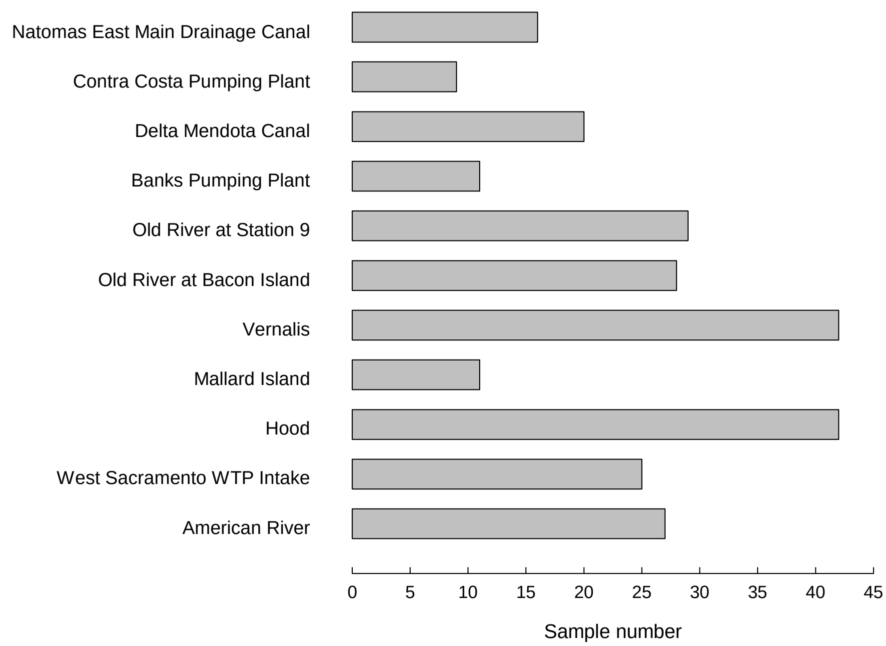
Table A-1 Summary of converted TOC by combustion at 14 stations

Although the above method works reasonably well for this particular data set, the equation cannot be applied for water samples collected at agricultural drainage sites. The data set does not include samples from drainage returns, and it is favorably biased toward samples collected during the wet months. However, no TOC from agricultural drainage returns needed to be converted during the 3-year reporting period.

Table A-1 Summary of converted TOC by combustion at 14 stations

Station	Total number of TOC by combustion	Number of converted TOC by combustion	Percent converted
American and Sacramento River stations			
American River at E.A. Fairbairn WTP	36	9	25
West Sacramento WTP Intake	36	6	17
Sacramento River at Hood	162	38	23
Sacramento River at Mallard Island	34	8	24
San Joaquin River stations			
San Joaquin River near Vernalis	156	40	26
San Joaquin River at Highway 4	34	7	21
Delta channel stations			
Old River at Station 9	38	5	13
Old River at Bacon Island	36	3	8
Diversion stations			
Banks Pumping Plant	37	3	8
Delta-Mendota Canal	27	1	4
Contra Costa Pumping Plant	29	5	17
Agricultural drainage stations			
Bacon Island Pumping Plant	25	0	0
Twitchell Island Pumping Plant	35	0	0
Urban drainage station			
Natomas East Main Drainage Canal	40	5	13
Total	725	130	

Figure A-1 Sample distribution by station and by month



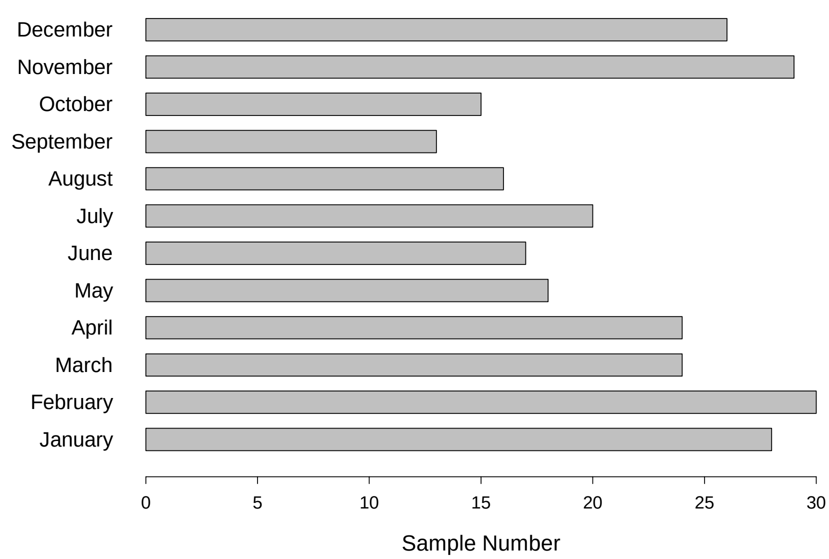
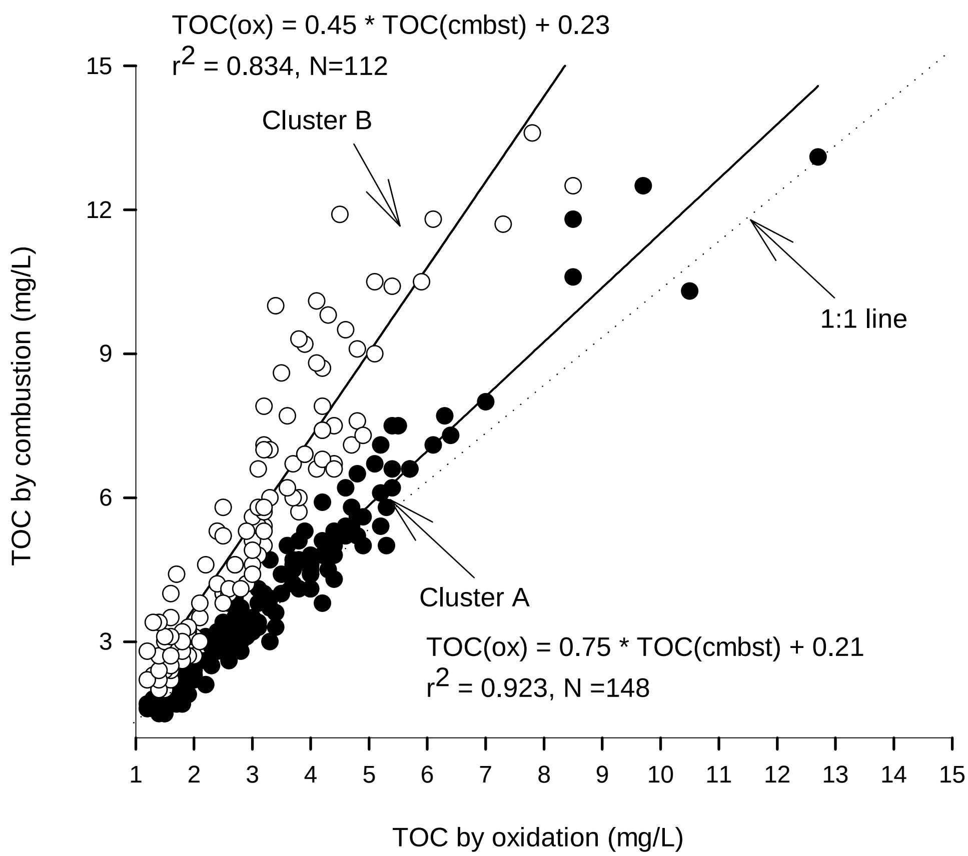


Figure A-2 TOC (combustion) vs. TOC (oxidation): Data clusters and regression equations for conversion



Appendix B
Report and Data in Electronic Format

This report and its data set are available electronically, either online or on CD-ROM.

You can find this report online at the Municipal Water Quality Investigations Program Web site: http://www.wq.water.ca.gov/mwq/index.htm. MWQI is a program within the Division of Environmental Services, a division of the California Department of Water Resources. All raw data are presented in MS Excel format. The report is provided as a portable document format (PDF). Acrobat Reader is required to view the report and is available free online.

For information about CD availability, contact Municipal Water Quality Investigations Program through its Web site or mail requests to the MWQI Program, P.O. Box 942836, Sacramento, CA 94236-0001.

California Department of Water Resources home page has links to DWR Web sites.
wwwdwr.water.ca.gov/

Municipal Water Quality Investigations
Rich Breuer,
Program Manager

Fengmao Guo,
Environmental Scientist